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54 A method for the oligomerization of C₆-olefins

57 In a method for the oligomerization of C₆-olefins with a reaction mixture that contains C₆-olefins on a solid bed catalyst that contains nickel, the reaction on the solid bed catalyst is performed through a conversion to form oligomerized C₆-olefins of not more than 30% by weight in relation to the reaction mixture.

Description

The invention concerns a method for the oligomerization of C₆-olefins, particularly for the production of C₁₂-olefins by way of a dimerization.

Methods for the oligomerization of olefins are known. DE-A-43 39 713 describes a method for the oligomerization of olefins to form highly linear oligomers. In that method, C₂₋₆-olefins are reacted at an increased pressure and increased temperature on a solid bed catalyst, in which case the applied catalyst contains between 10 and 70% by weight nickel oxide, between 5 and 30 % by weight titanium dioxide and/or zircon dioxide, between 0 and 20% by weight aluminum oxide as the substantially active components and silicon dioxide as the remaining components.

US 4,959,491 describes a method for the dimerization of C₆-olefins to form C₁₂-olefins that can be used for the production of tensides. The catalysts used consist of catalysts containing nickel such as hexafluoroaceto acetyl nickel cyclo-octadiene.

DE-A-39 14 817 describes a method for the oligomerization of C₂₋₈-olefins, in which case the reaction is achieved with nickel-exchanged montmorillonite, a nickel aluminum silicon-oxide catalyst or with molecular sieves impregnated with nickel or with zeolite. Prior to the catalytic reaction, the olefin mixture to be used is passed across a molecular sieve.

The known methods exhibit the disadvantage that the time of exposure of the catalyst is often too short. The catalyst is affected by higher oligomers in particular and thus loses its activity level.

The task of this invention consists in the development of a method for the oligomerization of C₆-olefins that does not exhibit the disadvantages of the known methods.

In accordance with the invention, the task is solved with a method for the oligomerization of C₆-olefins using a reaction mixture that contains C₆-olefins on a solid bed catalyst that contains nickel, in which case the reaction on the solid bed catalyst is performed with a conversion to form oligomerized C₆-olefins of not more than 30% by weight in relation to the reaction mixture.

In that regard, the reaction on the solid bed catalyst is performed in a preferred manner at a reaction rate of between 10 and 30% by weight and particularly preferred of between 10 and 25% by weight in relation to the reaction mixture. A dimerization is basically the preferred oligomerization method.

According to the invention, it was found that the catalyst deactivation can be prevented and the dimer selectivity can be increased when the reaction rate on the catalyst varies within the range indicated. The method can be run in a continuous or non-continuous manner. In a preferred manner, it is run continuously in the liquid phase. The reaction rate then refers to the passage of the reaction mixture through the catalyst.

The reaction is preferably performed at a temperature range of between 30 and 300 °C and a pressure range of between 10 and 300 bar.

To achieve a high total reaction rate with this method, it is possible to return a part of the obtained and reacted reaction mixture after separating the oligomers. Very high total reaction rates can be obtained by properly setting the returned quantity of the reaction mixture. The term "oligomers" also includes dimers and high-boiling compounds.

The method in accordance with the invention makes it possible to realize a reaction rate of more than 90% with a simultaneous C₁₂-selectivity of more than 80%. The service life and exposure period of the catalyst are very much increased when maintaining the reaction rate on the catalyst as indicated in the invention (in relation to a single passage), since this suppresses the formation of high-boiling compounds that are deposited on the catalyst and may thus cause an activity level decrease.

C₆-olefins that can be used in accordance with the invention can be synthesized on a large scale using methods such as the propylene dimerization. The most important propylene dimerization methods used by the industry are indicated, for example, in A. Chauvel and G. Lefebvre, Petrochemical Process, Edition Technip (1989), pages 183 through 187, and F. Asinger "The Petrochemical Industry, Akademier-Verlag (1971), pages 278 through 299. The large-scale oligomerization is performed in a homogenous-catalytic or heterogenous-catalytic manner. Heterogenous catalysts that can be used here are listed, for example, in C.T. O'Connor et al., Catalysis Today, Vol. 6 (1990), pages 329 through 349.

In relation to the produced quantity, the dimerol-G method by IFP represents the most important homogenous-catalytic method. It is thoroughly described in Oil, Natural Gas and Coal, Journal 7/8, July/August 1990, pages 309 through 315. The product (e.g., "Dimate") obtained with this method exhibits the following average olefin composition:

C ₃	4% by weight
C ₆	73% by weight
C ₉	17% by weight
C ₁₂	4% by weight
C ₁₅₊	2% by weight

The C₆-fraction consists of

4-methyl pentene-1	0.9% by weight
2,3-dimethyl butene-1	2.3% by weight
4-methyl pentene-2-cis	3.1% by weight
4-methyl pentene-2 trans	21.7% by weight
2-methyl pentene-1	5.0% by weight
hexene-1	0.3% by weight

hexene-3-trans	4.4% by weight
hexene-3 cis	0.7% by weight
hexene-2-trans	13.6% by weight
2-methyl pentene-2	39.2% by weight
hexene-2-cis	3.7% by weight
2,3-dimethyl butene-2	4.8% by weight

Metathesis methods represent another source for C₆-olefins.

Catalysts that are generally known, have a low branching effect and contain nickel can be considered as catalysts such as those described, for example, in *Catalysis Today*, Vol. 6 (1990), pages 336 through 338, DE-A 43 39 713, US 5,169,824, DD 2 73 055, DE-A-20 51 402, EP-A-0 202 670, *Appl. Catal.* 31 (1987), page 259-266, EP-A-0 261 730, NL 8 500 459, DE-A-23 47 235, US 5,134,242, EP-A-0 329 305, US 5,146,030, US 5,073,658, US 5,113,034 and US 5,169,824.

According to a preferred example of the method in accordance with the invention, the oligomerization is performed in the liquid phase and with the use of the catalysts described in DE-A 43 39 713.

The catalysts described there generally consist of nickel oxide, silicon oxide, titanium oxide and/or zircon oxide and possibly also of aluminum oxide with a nickel oxide content of between 10 and 70% by weight, a titanium oxide and/or zircon oxide content of between 5 and 30% by weight, an aluminum oxide content of between 0 and 20% by weight and the rest consists of silicon dioxide that can be obtained by precipitating the catalyst mass at a pH-value of 5-9 by adding an aqueous solution containing nickel nitrate to an alkali water glass solution that contains titanium oxide and/or zircon oxide. Filtering, drying and tempering at between 350 and 650 °C.

The catalysts preferably and generally consist of between 10 and 20% by weight titanium dioxide, of between 0 and 10% by weight aluminum oxide, of between 40 and 60% by weight nickel oxide as main component and active component and the rest of silicon oxide.

Specially preferred catalysts have the composition 50% by weight NiO, 34% by weight SiO₂, 3% by weight Al₂O₃ and 13% by weight TiO₂. They contain just about no alkali (Na₂O content < 0.3% by weight).

The catalysts are arranged preferably in a solid bed and are thus used in the form of solid pieces such as in the form of tablets (5 mm x 5 mm, 5 mm x 3 mm, 3 mm x 3 mm), rings (7 mm x 7 mm x 3 mm, 5 mm x 5 mm x 2 mm, 5 mm x 2 mm x 2 mm) or strands (1.5 mm diameter, 3 mm diameter, 5 mm diameter).

In a preferred manner, the process in accordance with the invention is performed by reacting a hydrocarbon flow that is preferably in the liquid phase and contains n-hexene and/or methyl pentene across the above-mentioned catalysts containing Ni.

Examples of suitable C₆-hydrocarbons are mixtures with the following composition:

Paraffine	10 to 90% by weight
Olefin	10 to 90% by weight,

in which case the olefin fraction may have the following composition:

n-hexenes	preferably between 0.1 and 99.8% by weight
Methyl pentenes	preferably between 0.1 and 99.8% by weight
Dimethyl butenes	preferably between 0.1 and 99.8% by weight

Oxygen-containing compounds such as alcohols, aldehydes, ketones or ethers are removed appropriately through adsorption from the hydrocarbon flows used in the process - in a manner known from DE-A 39 14 817 - with the help of a protective bed such as a molecular sieve, aluminum oxides, solid substances containing aluminum oxide, aluminum phosphates, silicon dioxides, siliceous earth, titanium dioxides, zirconium dioxides, phosphates, adsorbing agents containing carbon, polymer-adsorbing agents or mixtures thereof.

The oligomerization reaction is run at temperatures of between 30 and 300 °C, preferably of between 80 and 250°C and particularly preferred of between 100 and 200°C, and at a pressure of between 10 and 300 bar, preferably of between 15 and 100 bar and particularly preferred of between 20 and 70 bar. The pressure is selected appropriately such that the mixture to be used is liquid at the set temperature. The reactor generally consists of a cylindrical reactor or shaft furnace through which the liquid reaction mixture flows from the top to the bottom. After leaving the single- or multi-stage reaction zone, the thus formed oligomers are in a generally known manner separated from the C₆-hydrocarbons that have not reacted (e.g., by distillation) and the (latter) are fully or almost fully returned (however, a certain purge to flush out inert substances like hexane is always required).

A special characteristic of the reaction in accordance with the invention consists in the possibility to perform the process adiabatically in a shaft furnace, since the heat of reaction in the reactor can be controlled at any level by diluting the hexene with the returned flow and by selecting the quantity and temperature of this flow. In comparison to a described isothermal method, the adiabatic process substantially reduces equipment cost.

In accordance with a n example of the invention and prior to the reaction, the mixture to be used can be fractionated in a column (K) to separate the C₆-olefins and oligomers (C₇₊-hydrocarbons), the C₆-olefins can be piped to the reaction unit (C1), the reacted mixture can be returned to the column (K1) and the oligomers (C₇₊-hydrocarbons) can be transferred outward.

According to a further example and after the reaction, the reacted mixture can be fractionated in a column (K1) to separate the C₆-olefins and oligomers, the C₆-olefins can be returned to the reaction unit (C1) and the oligomers can be transferred outward.

The two methods described above are shown schematically in Figure 1a and 1b in the enclosed drawing.

The reference numbers shown there indicate the following:

- F1: Protective bed
- C1: Reactor
- K1: Column
- F: Feed
- P: Purge
- D: Distillate
- s: Sump

The protective bed (F1) is used to remove catalyst poisons (mainly S-N-O-containing hydrocarbons).

Separating the oligomers is achieved in a known manner through a fractionated distillation to separate the desired dodecenes. The sweet C₁₃₊-fraction exhibits a high blending value with respect to a mixing into a diesel fuel pool. Particularly preferred is the application of this C₁₃₊-fraction as a mixing component for diesel fuel after the olefins have been converted to paraffins by way of a hydration. This measure yields a higher cetane number that is of great importance for the properties of this diesel fuel. The hydration may be achieved with any of the methods known to the prior art.

The dodecenes obtained from the hexene dimerization can be processed further to form tensides.

The following examples explain the method in accordance with the invention in more detail:

Examples

The test unit consisted of the following equipment (process chart according to Figure 1):

- Adsorption unit to remove the catalyst poisons (F1; volume of approximately 50 liters)
- Adiabatic reactor (C1, volume of approximately 40 liters, length: 8 m, diameter: 80 mm)
- Distillation column (K1) for the separation of unreacted C₆-olefins and the formed oligomers [C₁₂]

The catalyst consisted of a material that was produced in accordance with DE-A 43 39 713 to form 5 mm x 5 mm tablets. Composition of the active components in % by weight: 50% by weight NiO, 13% by weight TiO₂, 34% by weight SiO₂, 3% by weight Al₂O₃.

The adsorption unit consisted of an aluminum oxide with a large surface such as Selexsorb[®] manufactured by Alcoa.

Example 1

The mixture to be used consisted of a hydrocarbon mixture with the following composition:

C ₃	4% by weight
C ₆	73% by weight
C ₉	17% by weight
C ₁₂	4% by weight
C ₁₅₊	2% by weight

The C₆-fraction consisted of the following components:

4-methyl pentene-1	0.9% by weight
2,3-dimethyl butene-1	2.3% by weight
4-methyl pentene-2 cis	3.1% by weight
4-methyl pentene-2 trans	21.7% by weight
2-methyl pentene-1	5.0% by weight
hexene-1	0.3% by weight
hexene-3 trans	4.4% by weight
hexene-3 cis	0.7% by weight
hexene-2 trans	13.6% by weight
2-methyl pentene-2	39.2% by weight
hexene-2 cis	3.7% by weight
2,3-dimethyl butene-2	4.8% by weight

The hydrocarbon mixture was supplied to column K1 at a rate of 5.1 kg/h (Figure 1). The following conditions were set in the test unit:

<u>Adsorption section:</u>	
Pressure (bar)	15
Temperature (°C)	35
Throughput (kg/h)	18.8
<u>Synthesis section:</u>	
Catalyst quantity (kg)	25
Pressure (bar)	15
Inlet temperature (°C)	100
Outlet temperature (°C)	139
Throughput (kg/h)	18.8
<u>Distillation section:</u>	
Pressure (bar)	1
Temperature / head (°C)	35
Temperature / sump (°C)	185
Quantity (kg/h)	23.9
Distillate (kg/h)	19.0
Purge (kg/h)	0.2
Sump (kg/h)	4.9

The following result was achieved:

Composition

Flow	C ₃	C ₆	C ₉	C ₁₂	C ₁₅₊	Total C ₉₊
Mixture K1 = reactor discharge	1.7	78.1	3.7	13.4	3.1	20.2
Distillate K1	2.1	97.9	< 0.1	< 0.1	< 0.1	-
Sump K1	< 0.1	0.4	17.7	64.7	17.2	99.6

This yields a reaction rate of 94.7% for the C₆-olefins and a C₁₂-selectivity of 83.6% (in relation to the reacted C₆-olefins).

Example 2

The mixture to be used consisted of a hydrocarbon mixture with the following composition:

C ₅	0.1% by weight
C ₆	98.7% by weight
C ₇	1.2% by weight

The C₆-fraction consisted of the following components:

4-methyl pentene-1	<0.1% by weight
2,3-dimethyl butene-1	<0.1% by weight
4-methyl pentene-2 cis	<0.1% by weight
4-methyl pentene-2 trans	<0.1% by weight
2-methyl pentene-1	<0.1% by weight
hexene-1	<0.1% by weight
hexene-3 trans	90% by weight
hexene-3 cis	10% by weight
hexene-2 trans	<0.1% by weight
hexene-2 cis	<0.1% by weight
2-methyl pentene-2	<0.1% by weight
2,3-dimethyl butene-2	<0.1% by weight

The hydrocarbon mixture was supplied to filter F1 at a rate of 3.20 kg/h (Figure 2). The following conditions were set in the test unit:

<u>Adsorption section:</u>	
Pressure (bar)	10
Temperature (°C)	35
Throughput (kg/h)	3.20
<u>Synthesis section:</u>	
Catalyst quantity (kg)	25
Pressure (bar)	10
Inlet temperature (°C)	100
Outlet temperature (°C)	133
Throughput (kg/h)	15.75
<u>Distillation section:</u>	
Pressure (bar)	1
Temperature / head (°C)	45
Temperature / sump (°C)	182
Quantity (kg/h)	15.75
Distillate (kg/h)	12.60
Purge (kg/h)	0.05
Sump (kg/h)	3.15

The following result was achieved:

Composition

Flow	C ₅	C ₆	C ₇₋₁₁	C ₁₂	C ₁₃₊	Total C ₇₊
Mixture K1 = reactor discharge	< 0.1	806	0.4	15.7	3.3	19.4
Distillate K1	0.1	99.9	< 0.1	< 0.1	< 0.1	-
Sump K1	< 0.1	0.4	1.3	81.2	17.1	99.6

This yields a reaction rate of 98.4% for the C₆-olefins and a C₁₂-selectivity of 82.6% (in relation to the reacted C₆-olefins).

Patent claims

1. A method for the oligomerization of C₆-olefins with the reaction of a reaction mixture that contains C₆-olefins on a solid bed catalyst that contains nickel, **characterized by the fact that** the reaction on the solid bed catalyst is performed through a conversion to form oligomerized C₆-olefins of not more than 30% by weight in relation to the reaction mixture.
2. A method in accordance with claim 1, characterized by the fact that the reaction on a solid bed catalyst to form oligomeric C₆-olefins is performed at 10 to 30% by weight in relation to the reaction mixture.
3. A method in accordance with claim 1 or 2, characterized by the fact that the oligomerization basically consists of a dimerization.
4. A method in accordance with one of claims 1 through 3, characterized by the fact that the solid bed catalyst containing nickel has between 10 and 70% by weight nickel oxide, between 5 and 30% by weight titanium dioxide and/or zircon dioxide, between 0 and 20% by weight aluminum oxide as the substantially active components and silicon dioxide as the remaining component.
5. A method in accordance with one of claims 1 through 4, characterized by the fact that the process is run at a pressure ranging between 10 and 300 bar and at a temperature ranging between 30 and 300 °C.
6. A method in accordance with one of claims 1 through 5, characterized by the fact that the process is run continuously in the liquid phase.
7. A method in accordance with claim 6, characterized by the fact that the process is run adiabatically in a shaft furnace and that a part of the reacted mixture is returned to the reaction process.
8. A method in accordance with one of claims 1 through 7, characterized by the fact that the mixture to be used can be fractionated prior to the reaction in a column to separate the C₆-olefins and oligomers, the C₆-olefins can be piped to the reaction process, the reacted mixture can be returned to the column and the oligomers (C₇₊-hydrocarbons) can be transferred outward.
9. A method in accordance with one of claims 1 through 7, characterized by the fact that the reacted mixture is fractionated after the reaction in a column to separate the C₆-olefins and oligomers, the C₆-olefins are returned to the reaction process and the oligomers are transferred outward.
10. A method in accordance with one of claims 1 through 9, characterized by the fact that the reaction mixture is passed across a protective bed prior to the reaction process.

DRAWING PAGE 1

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